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Isolation and characterization of the tetralithium salt of [5]radialene tetraanion stabilized by silyl groups

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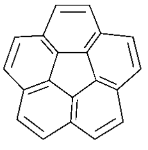
Persilyl-substituted [5]radialene 3 was reacted with lithium metal in THF to yield dark red crystals of the tetralithium salt of tetraanion 4 with a novel ten-center, fourteen π-electron system stabilized by silyl groups.

Polyanions with extended π-electron systems have attracted considerable interest owing to their unique structures and electronic properties.[1,2] However, polyanions of polycyclic hydrocarbons have only rarely been observed and they are one of the most attractive synthetic targets. Corannulene **1** having a twenty π-electron system has a doubly-degenerate, low-lying LUMO that can accept up to four electrons to form corannulene tetraanion.[3] Scott *et al.* reported on the interesting dimer structure of the tetralithium salt of corannulene tetraanion and its derivatives in solution.[4] [5]Radialene **2** with a cross-conjugated ten π-electron system possesses a central unit of corannulene. However, to the best of our knowledge, there have been no studies on the anion species of [5]radialene derivatives. Herein, we report the first successful isolation, characterization and molecular structure of the tetralithium salt of the [5]radialene tetraanion derivative with a novel ten-center, fourteen π-electron system stabilized by silyl groups.



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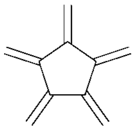

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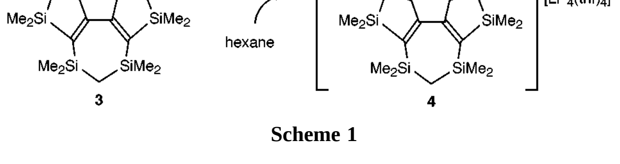
Reduction of **3**[5] with excess lithium metal in dry, oxygen free THF at room temperature led to the formation of a dark red solution of the tetraanion of **3** (Scheme 1). Crystallization from hexane afforded air- and moisture-sensitive dark red crystals of the tetralithium salt **4**.†

The molecular structure of **4** was determined by X-ray diffraction, as shown in Fig. 1.‡ The tetralithium salt (**4**) is monomeric and forms contact ion pairs (CIPs) in the crystals. One THF molecule is coordinated to each lithium ion. All four lithium ions are bonded to four quaternary carbon atoms of the [5]radialene π-skeleton as well as to the oxygen atoms of THF. Li1 and Li2 are located above and below the adjacent seven-membered rings (denoted **A** for the C1–C5–C10–Si7–CH_2-Si8-C6 ring and **B** for the C1–C2–C7–Si2–CH_2–Si1–C6 ring, respectively), whereas Li3 is located below the isolated seven-membered ring (denoted **C** for the C4–C3–C8–Si4–CH_2-Si5-C9 ring). The remaining Li4 is situated above one of the two silacyclopentadiene rings (denoted **D** for the C2–C3–C8–Si3–C7 ring and **E** for the C5–C4–C9–Si6–C10 ring, respectively). The distances between lithium and carbon atoms range from 2.10(1) to 2.44(2) Å (av. 2.23 Å). The two seven-membered rings **A** and **B** have highly twisted conformations about the C1–C6 bond, whereas the other seven-membered ring **C** and the two five-membered rings **D** and **E** are almost coplanar.



Scheme 1

A comparison of the structural parameters of neutral molecule **3**[5] and tetraanion **4** is quite interesting. The ten carbon atoms (C1–C10) which constitute the π-electron system of the skeleton of **4** are almost coplanar as a consequence of the delocalization of the negative charge. The C1–C6 distance in **4** [1.523(8) Å] is considerably elongated by 0.148 Å relative to that of **3** [1.375(4) Å]. The C3–C8 and C4–C9 distances in **4** are also elongated by 0.143 and 0.066 Å, compared with those of **3** [1.363(4) Å]. The C2-C7 and C5-C10 distances in **4** are also stretched by 0.059 and 0.044 Å, relative to those of **3** [1.362(4) and 1.363(4) Å]. By contrast, the C3–C4 distance in **4** [1.377(8) Å] is remarkably shortened by 0.106 Å with respect to that of **3** [1.483(4) Å]. The C1–C2 and C1–C5 distances in **4** are shortened by 0.056 and 0.044 Å compared with those in **3** [1.506(4) and 1.485(4) Å]. These structural features are reflected by the LUMO and next LUMO of **3** (Fig. 2).[6] That is, in the LUMO of **3**, the exocyclic bonds are all antibonding, whereas the endocyclic bonds are all bonding. In the next LUMO of **3**, the exocyclic bonds, and C2–C3 and C4–C5 bonds are antibonding, while the C1–C2, C1–C5 and C3–C4 bonds are bonding.

The central five-membered ring (C1–C2–C3–C4–C5) of **4** has an almost planar structure, as determined by the sum of the bond angles (539.9°). However, this five-membered ring does not form an equilateral pentagon, as observed in the dilithium salt of hexasilylfulvene dianion with a six-center, eight π-

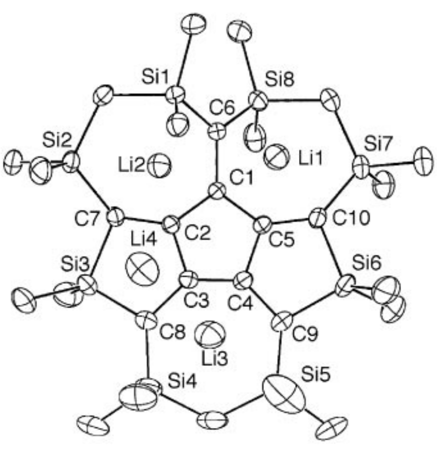
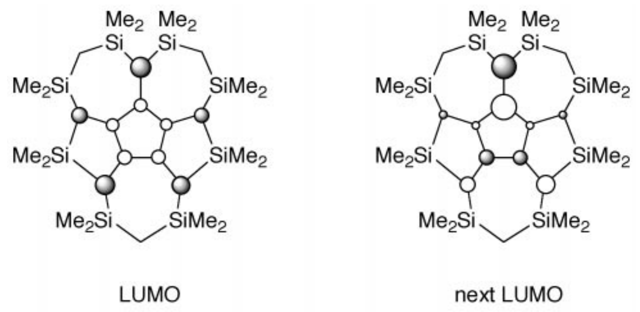


Fig. 1 Structure of **4** (THF and hydrogen atoms are omitted for the clarity). Selected bond distances (Å) are: C1–C2 1.450(7), C1–C5 1.441(8), C1–C6 1.523(8), C2–C3 1.484(8), C2–C7 1.421(8), C3–C4 1.377(8), C3–C8 1.506(8), C4–C5 1.526(8), C4–C9 1.429(8), C5–C10 1.407(8), C6–Si1 1.824(6), C6–Si8 1.815(6), C7–Si2 1.830(6), C7–Si3 1.898(6), C8–Si3 1.823(7), C8–Si4 1.798(7), C9–Si5 1.812(7), C9–Si6 1.829(7), C10–Si6 1.876(6), C10–Si7 1.841(6).



LUMO

next LUMO

Fig. 2 Schematic representation of LUMO and next LUMO of **3** calculated by PM3.

electron system,[7] and the tetralithium salt of octasilyltrimethylenecyclopentene tetraanion with an eight-center, twelve π-electron system.[2] This suggests that the [5]radialene tetraanion **4** has no aromatic character resulting from the cyclopentadienide ion. The bond lengths of the Si–C (quaternary carbons) bonds of **4** (av. 1.835 Å) are shorter than those of **3** (av. 1.873 Å) due to delocalization of the negative charge onto the silicon centers by $p\pi$–σ^* conjugation.

The NMR data of **4** in toluene-d_8 indicate formation of highly symmetric CIPs with C_2 groups symmetry, the C1–C6 bond being a two-fold axis. The four methyls of two $SiMe_2$ groups and the two hydrogen atoms of CH_2 for rings **A** and **B** are magnetically nonequivalent, due to the fixed five- and seven-membered rings. On the other hand, the two hydrogen atoms of CH_2 for ring **C** are magnetically equivalent. Thus, the ^{1}H NMR spectrum of **4** in toluene-d_8 reveals the presence of eight signals for the methyl groups, two doublets for the ring **A** and **B** methylene groups with a geminal coupling constant of 13.2 Hz, and one singlet for the ring **C** methylene group. In the ^{29}Si NMR spectrum, four signals are observed at δ −20.1, −16.7, −15.0, and 18.5, which are shifted to higher field in comparison to those of **3** (δ −12.0, −10.0, −8.4 and 30.9). The ^{13}C NMR spectrum shows six signals for quaternary carbon atoms at δ 15.1, 40.8, 81.0, 93.1, 131.8 and 178.9. The signal appearing at δ 15.1 is assignable to the C6 carbon atom, which is considerably up-field shifted relative to that of **3** (δ 164.7) by $\Delta\delta$ −149.6 ppm. The other exocyclic carbons (C7, C8, C9 and C10) are also shifted to higher field by the four electron reduction (δ 40.8 and 81.0 for **4**; δ 163.2 and 172.0 for **3**). Apparently, the negative charge is largely delocalized over the five exocyclic carbon atoms in the π-skeleton of **4** and is stabilized by the eight silyl groups. Interestingly, the ^{6}Li NMR spectrum of **4** displays only one signal at δ −0.18. This indicates that the four Li^+ ions of **4** are not fixed to the π-skeleton, but are fluxional; the four Li^+ ions are migrating over the π-skeleton of [5]radialene on the NMR time scale.[8]

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Notes and references

† The crystals of **3** (21 mg, 0.033 mmol) and lithium metal (30 mg, 4.3 mmol) were placed in a reaction tube with a magnetic stirrer. After degassing the tube, dry oxygen-free THF (0.8 ml) was introduced by vacuum transfer and stirred at room temperature to give a dark red solution of **4** within 1 h. After the solvent was removed *in vacuo*, degassed hexane was introduced by vacuum transfer. After the lithium metal had been removed from the tube, the solution was cooled to afford dark red crystals of **4** quantitatively; δ_H(300 MHz, C_7D_8) −0.15 (d, J 13.2, 2H, CH_2), −0.11 (s, 6H, CH_3), 0.14 (s, 2H, CH_2), 0.28 (s, 6H, CH_3), 0.30 (s, 6H, CH_3), 0.33 (s, 6H, CH_3), 0.35 (s, 6H, CH_3), 0.36 (s, 6H, CH_3), 0.49 (s, 6H, CH_3), 0.54 (d, J 13.2, 2H, CH_2), 0.62 (s, 6H, CH_3), 1.35 (br s, 16H, THF), 3.52 (br s, 16H, THF); δ_C(75.5 MHz, C_7D_8) 2.8 (CH_3), 5.6 (CH_3), 6.0 (CH_3), 6.6 (CH_3), 7.0 (CH_3), 7.3 (CH_3), 7.5 (CH_3), 7.7 (CH_3), 15.1 (C), 15.9 (CH_2), 16.5 (CH_2), 25.4 (THF), 40.8 (C), 66.6 (THF), 81.0 (C), 93.1 (C), 131.8 (C), 178.9 (C); δ_{Si}(59.6 MHz, C_7D_8) −20.1, −16.7, −15.0, 18.5; δ_{Li}(44.2 MHz, C_7D_8) −0.18.

‡ *Crystal data* for **4**: $C_{45}H_{86}Li_4O_4Si_8$, M = 943.63, monoclinic, a = 48.328(3), b = 13.470(1), c = 21.676(1) Å, β 115.003(3)°, V = 12788(1) Å^3, T = 180 K, space group $C2/c$, Z = 8, ρ_{calc} = 0.981 g cm^{-3}. Diffraction data were collected on a MacScience DIP2030K Image Plate Diffractometer employing graphite-monochromatized Mo–Kα radiation (λ = 0.71070 Å). The final R factor was 0.0775 (R_w = 0.2358) for 6138 reflections with $I > 3\sigma(I)$. Single crystals of **4** were obtained by crystallization from hexane, mounted in a glass capillary tube and transferred to the cold gas stream of the diffractometer. The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Some of the carbon atoms of the THF molecules have elongated thermal ellipsoids due to disorder. CCDC 182/1394. See http://www.rsc.org/suppdata/cc/1999/1981/ for crystallographic data in .cif format.

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5 Persilylated [5]radialene **3** was obtained by the intramolecular reaction of hexadecamethyl-3,6,8,11,14,16,19,21–octasilacycloicosa-1,4,9,12,17-pentayne with an excess of $[Mn(CO)_3(C_5H_4Me)]$ by irradiation (λ > 300 nm) in refluxing THF, see: T. Matsuo, H. Fure and A. Sekiguchi, *Chem. Lett.*, 1998, 1101.

6 PM3 calculation was performed with geometry optimization. The geometry of **3** by X-ray diffraction was successfully reproduced by PM3 calculation.

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8 As the temperature was lowered, the ^{6}Li NMR signal broadened and eventually yielded two very sharp signals at δ −0.55 and 0.08 with the same intensity at 187 K. This can be explained by assuming that the two Li^+ ions (Li1 and Li2) are fixed to the seven-membered rings (**A** and **B**), whereas the other two Li^+ ions (Li3 and Li4) are still fluxional over two five-membered rings (**D** and **E**) and one seven-membered ring (**C**). Since the latter three rings are almost coplanar, the fluxional behavior of the two Li^+ ions (Li3 and Li4) is not hindered even at 187 K. The possibility of producing a solvent-separated ion pair (SSIP) in toluene-d_8 is unlikely. The ^{6}Li NMR in THF-d_8 gave broad and complex signals.

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